



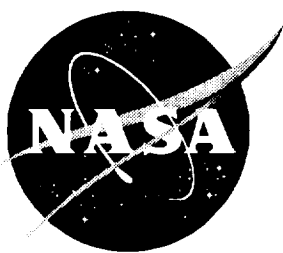
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Investigation of Oxygen-Induced Quenching of Phosphorescence in Photoexcited Aromatic Molecules by Positron Annihilation Spectroscopy

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Symbols

A	constant
I_i	intensity of i th component
Mg.OEP	magnesium octaethyl porphyrin
Pt.OEP	platinum octaethyl porphyrin
$P(S_i), P(T_i)$	singlet and triplet states of metalloporphyrin molecules
R	$= \frac{S_{\text{with light}}}{S_{\text{no light}}}$
S	Doppler parameter, $\frac{\text{Area of central section of peak}}{\text{Total area of peak}}$
T_i	i th triplet state
$X(\text{O}_2)$	mole fraction of oxygen in surrounding medium
τ_i	lifetime of i th component
Superscript:	
*	excited state of complex

Abstract

Platinum octaethyl porphyrin (Pt.OEP) is an efficient phosphor under ultraviolet excitation. The phosphorescent triplet state $P(T_1)$ is readily quenched by the oxygen O_2 molecules. This phenomenon is being utilized as the basis for global air pressure measurements in aerodynamic facilities at various laboratories. The exact mechanism by which O_2 molecules quench the $P(T_1) \rightarrow P(S_0)$ transitions is still unknown. The diamagnetic singlet states $P(S_n)$, which feed $P(T_1)$ states via intersystem crossings, would presumably not be affected by O_2 . It must be only the magnetic $P(T_1)$ states, which can interact with the paramagnetic O_2 molecules, that are affected. However, our positron lifetime and Doppler broadening studies suggest the formation of $O_2 \cdot P(S_n)$ complexes which can also eventually reduce the population of the $P(T_1)$ states (i.e., quench phosphorescence). This reduction is possible because higher triplet states in (Pt.OEP) are admixed with the $P(S_n)$ states via spin orbit interactions. The experimental procedures and the results of various measurements are presented in this paper.

Introduction

The basic ring structure of a porphyrin molecule is characterized by a 4-fold symmetry, including 4 nitrogen atoms directed towards the center. When the 8 exohydrogens in it are replaced by CH_3CH_2 groups, the molecule becomes octaethyl porphyrin. If the 2 central hydrogens are also replaced by metal atoms, the molecule becomes a metalloporphyrin. These metal atoms can have significant effects on the electronic and optical properties of the parent molecules. (See ref. 1.) Among the most widely studied metalloporphyrins are platinum octaethyl porphyrin (Pt.OEP) molecules. Figure 1 shows the chemical structure of a platinum octaethyl porphyrin molecule; figure 2 shows its schematic energy level diagram and decay scheme.

Under UV irradiation, the Pt.OEP molecule is excited to a higher singlet state which decays very quickly to the lowest excited singlet state. From this

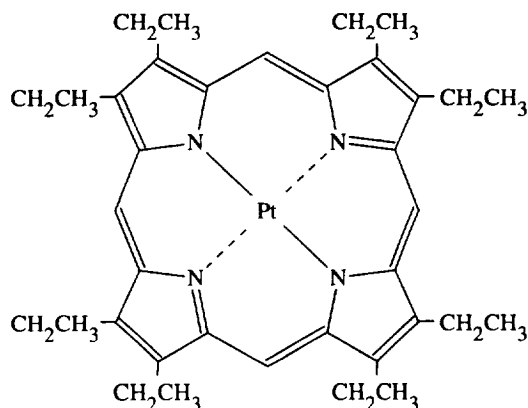


Figure 1. Chemical structure of platinum octaethyl porphyrin (Pt.OEP).

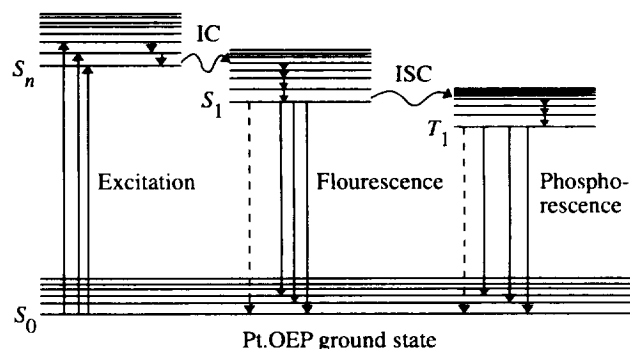
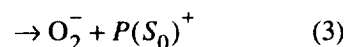
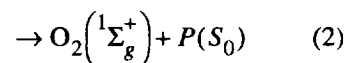
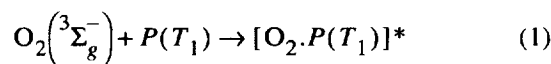


Figure 2. Typical level scheme for a metalloporphyrin molecule.

singlet state, the molecule can decay to the ground state by a radiative or nonradiative transition or internally convert to the lowest excited triplet state. This triplet state can either be re-excited to the higher singlet state by thermal excitation or collision with another triplet state molecule or phosphoresce to the ground state with a lifetime of the order of 100 μ sec. In references 1 and 2, the presence of oxygen molecules near the photoexcited Pt.OEP molecules has been reported to lead to the quenching of the phosphorescence in them. When an oxygen molecule comes in contact with a Pt.OEP molecule in its lowest excited triplet state, $P(T_1)$, one of the following reactions can occur:



Reaction (3) is possible only in the condensed state of Pt.OEP formulation. All these reactions result in the

reduction of phosphorescence from the $P(T_1)$ state. It is well recognized that the $P(S_n)$ states of the aromatic molecules are admixed with the higher triplet states. (See ref. 1.) Thus, the paramagnetic oxygen (O_2) molecule will not necessarily be repelled by the mostly diamagnetic $P(S_n)$ states. When an (O_2) molecule comes in contact with a $P(S_1)$ molecule, it can form a transient $[O_2.P(S_1)]^*$ complex. Such a complex is expected to be considerably higher in energy than the $P(S_1)$ state. As seen in figure 3, $P(S_1)$ occurs at 2.34 eV above the ground state, $P(S_0)$. Because of the competing radiationless transitions from it, the formation of $[O_2.P(S_1)]^*$ complex will also result in a net reduction in the population of $P(T_1)$ state and hence phosphorescence from it. Currently, the $[O_2.P(T_1)]^*$ interaction alone is believed to be responsible for the reduction in the $P(T_1) \rightarrow P(S_0)$ radiative transitions. No reason exists why $[O_2.P(S_1)]^*$ complex formation, which can also reduce the population of the $P(T_1)$ state and hence the phosphorescence intensity, cannot also play a role. The purpose of this investigation is to determine whether $[O_2.P(S_1)]^*$ interactions play a role in the O_2 -induced quenching process of $P(T_1) \rightarrow P(S_0)$ phosphorescence in Pt.OEP molecules.

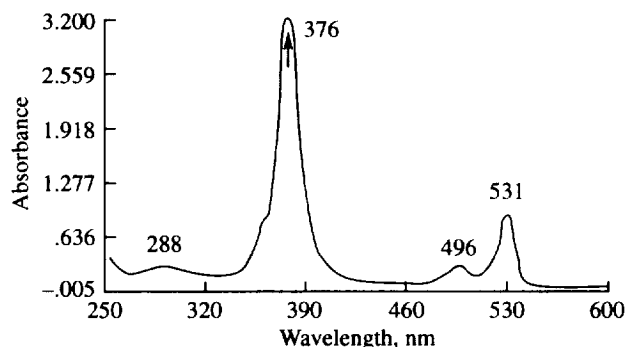


Figure 3. Absorption spectrum of Pt.OEP molecules dissolved in CH_2Cl_2 .

Experimental Procedures and Results

Two types of metalloporphyrins were used in this study:

1. Platinum octaethyl porphyrin, Pt.OEP
2. Magnesium octaethyl porphyrin, Mg.OEP

Pt.OEP has a reported phosphorescence quantum yield of approximately 90 percent. (See ref. 3.) Figure 4 shows the emission spectrum of this molecule excited at 3760 Å. Clearly, the phosphorescence peak at 6445 Å dominates the spectrum.

Mg.OEP has a reported phosphorescence quantum yield of less than 2 percent. (See ref. 1.) Figure 5 shows

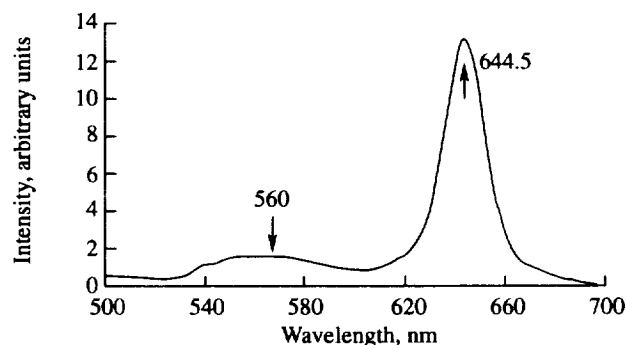


Figure 4. Emission spectrum from Pt.OEP molecules dissolved in CH_2Cl_2 excited at 3760 Å.

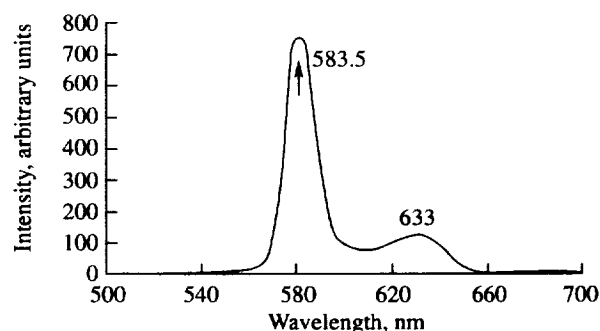


Figure 5. Emission spectrum from Mg.OEP molecules dissolved in CH_2Cl_2 excited at 4010 Å.

the emission spectrum of this molecule excited at 4010 Å. Clearly, the phosphorescence is very weak and the fluorescence peak at 5835 Å dominates the spectrum. The low phosphorescence yield of Mg.OEP may be due to the reduced population, or an even lower energy, of the $P(T_1)$ state in it; it may also be due to the lighter mass of the central substituent magnesium atom (ref. 1). However, Mg.OEP was selected for this study mainly on the assumption that the excited singlet ($S = 0$) states in it are less admixed with the higher triplet ($S = 1$) states.

The metalloporphyrin (M.OEP) targets were prepared by air spraying a solution of (M.OEP) molecules in trichloroethane ($C_2H_3Cl_3$) on thin aluminum substrates. The $C_2H_3Cl_3$ molecules evaporated quickly leaving the M.OEP molecules adhered to the aluminum substrates.

Positron lifetime and Doppler broadening measurements were made in M.OEP molecular films, spray coated on both sides of 250- μ m-thick aluminum substrates. The substrates were shaped into two 5-cm-high concentric cylinders of diameter 2.50 and 3.80 cm, respectively. The aluminum cylinders were enclosed in a glass cylinder 7.5 cm high and 7.5 cm in diameter, which could be pumped down to 10^{-4} torr. A 50- μ Ci Na^{22}

positron source deposited on a steel needle tip was located at the center of the aluminum cylinders. The phosphor films were photoexcited with ultraviolet radiation from a xenon short arc lamp located above the glass cylinder.

Positron lifetime measurements were made with a standard fast-fast coincidence system, whose resolution time is of the order of 280 psec. The Doppler broadening measurements were made with a high-purity germanium detector, whose full width at half maximum (FWHM) resolution for Bi^{207} radiation is 1.28 keV. Both types of measurements were made *with* and *without* ultraviolet excitation of the phosphor molecules in vacuum, N_2 , O_2 , and air media at room temperature. Figure 6 shows the experimental setup for positron annihilation measurements.

The positron lifetime results in the Pt.OEP phosphor are summarized in table I. The contributions of aluminum substrates and the glass cylinder have not been subtracted from these data; however, these contributions are not expected to change with the UV irradiation. The Doppler broadening results in Pt.OEP and Mg.OEP phosphors are summarized in tables II(a) and (b), respectively. Figure 7 illustrates the Doppler broadening results.

Discussion

An examination of the data in table I shows that UV irradiation has little effect on the positron lifetime spectra in any one of the media surrounding the Pt.OEP-coated aluminum cylinders. In particular, even a pure oxygen

environment does not seem to affect positron lifetimes. This is surprising because positronium (Ps) formation is possible at the $[\text{O}_2.P(S_1)]^*$ sites. It may, however, be due to the fact that the Ps atom formed at the $[\text{O}_2.P(S_1)]^*$ complex will be readily quenched by the paramagnetic O_2 molecule released in the process. (See ref. 4.) This fast positronium decay component will not be resolvable from the prompt annihilation component in the positron lifetime spectrum. Similar behavior was observed in lifetimes in Mg.OEP molecular coatings. However, Ps formation in photoexcited Mg.OEP molecules is not possible due to insufficient energy. Thus, UV irradiation is not expected to have any effect on the positron lifetime spectra in Mg.OEP coatings in any medium surrounding them.

The Doppler broadening data in table II exhibit two interesting features: (1) Doppler broadening parameter S in Pt.OEP molecules under UV irradiation increases steadily as the partial pressure of oxygen in the surrounding medium increases and (2) UV irradiation does not measurably affect Doppler broadening parameters in Mg.OEP molecules in any of the surrounding media.

These data are consistent with a lower excitation energy for $P(S_1)$ state in Mg.OEP molecules, as seen in figure 8, and even lower probability for $[\text{O}_2.P(S_1)]^*$ complex formation in them. Under these conditions, Ps atoms are not formed at $P(S_1)$ sites in Mg.OEP molecules, and therefore, the Doppler parameter should not be affected, as is seen in figure 7(a). The excitation energy of the $P(S_1)$ state and the probability of $[\text{O}_2.P(S_1)]^*$ complex formation in Pt.OEP, on the other hand, are quite

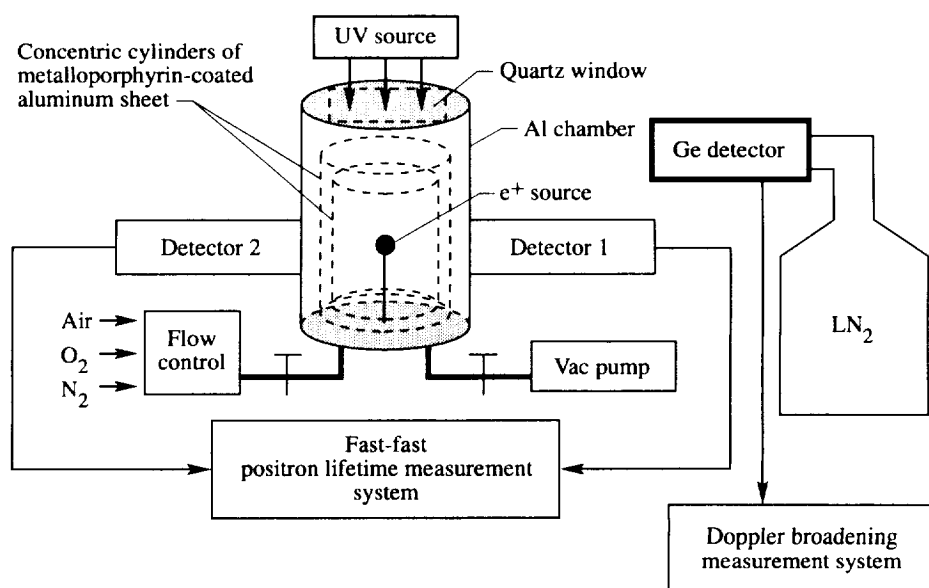
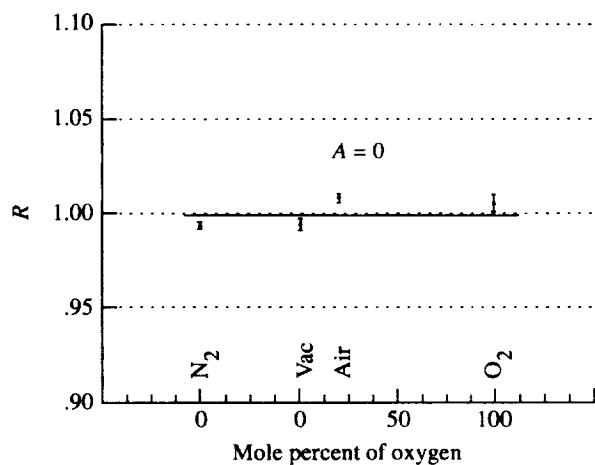
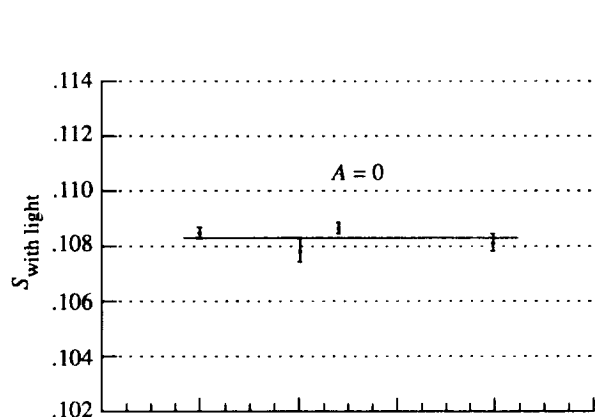
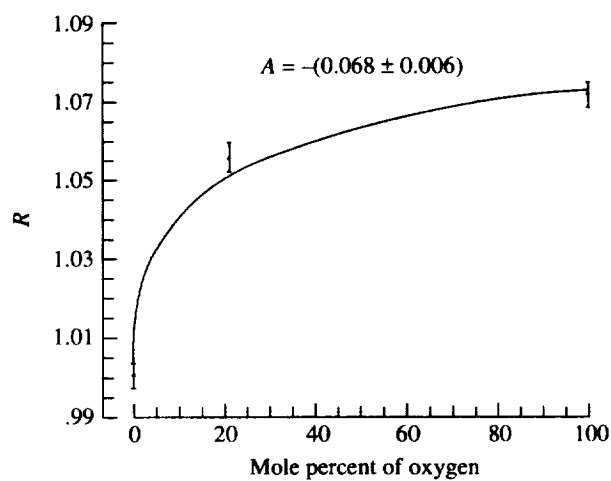
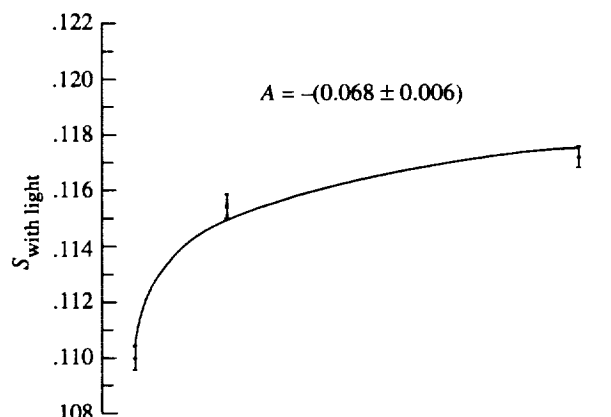


Figure 6. Schematic diagram for positron annihilation studies in metalloporphyrins.



(a) Mg.OEP molecules.



(b) Pt.OEP molecules.

Figure 7. Variation of Doppler broadening parameters as function of mole percent of oxygen in surrounding medium. Solid line is least squares fit for $S(X) = S(X=0) \{1 + A[X(O_2)]^{0.25}\}$.

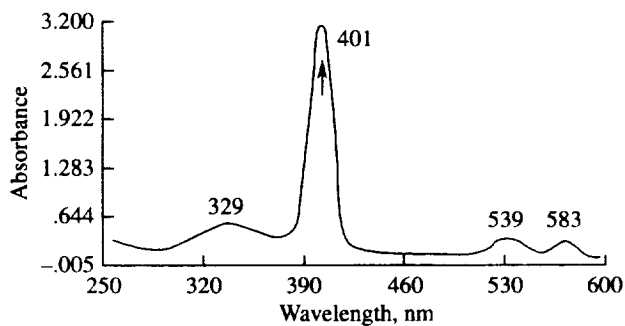


Figure 8. Absorption spectrum of Mg.OEP molecules dissolved in CH_2Cl_2 .

Table I. Positron Lifetime Results in (Pt.OEP)

Surrounding medium	τ_1/I_1 , psec/percent	τ_2/I_2 , psec/percent	τ_3/I_3 , psec/percent
(a) Without UV irradiation			
Vacuum	$246 \pm 2/87.0 \pm 0.6$	$781 \pm 32/8.7 \pm 0.4$	$3015 \pm 129/4.3 \pm 0.3$
Air	$251 \pm 1/89.8 \pm 0.4$	$870 \pm 44/6.1 \pm 0.4$	$2940 \pm 143/4.1 \pm 0.6$
Oxygen	$251 \pm 1/88.3 \pm 0.5$	$907 \pm 61/7.2 \pm 0.4$	$2977 \pm 96/4.4 \pm 0.3$
(b) With UV irradiation			
Vacuum	$245 \pm 2/86.8 \pm 0.8$	$776 \pm 44/8.8 \pm 0.5$	$3029 \pm 180/4.3 \pm 0.5$
Air	$242 \pm 1/88.9 \pm 0.4$	$869 \pm 41/7.1 \pm 0.3$	$3023 \pm 147/4.0 \pm 0.4$
Oxygen	$249 \pm 1/88.4 \pm 0.5$	$927 \pm 62/7.4 \pm 0.4$	$3026 \pm 116/4.2 \pm 0.3$

Table II. Doppler Broadening Data in Metallized Porphyrins

Surrounding medium	$S_{\text{no light}}$	$S_{\text{with light}}$	R
(a) Pt.OEP phosphor			
Vacuum	0.1086 ± 0.0005	0.1103 ± 0.0006	1.015 ± 0.005
Nitrogen	0.1099 ± 0.0004	0.1096 ± 0.0004	0.997 ± 0.004
Air	0.1093 ± 0.0006	0.1153 ± 0.0006	1.055 ± 0.005
Oxygen	0.1093 ± 0.0004	0.1171 ± 0.0004	1.072 ± 0.004
(b) Mg.OEP phosphor			
Vacuum	0.1086 ± 0.0007	0.1078 ± 0.0007	0.993 ± 0.006
Nitrogen	0.1092 ± 0.0004	0.1084 ± 0.0004	0.993 ± 0.004
Air	0.1077 ± 0.0004	0.1086 ± 0.0004	1.008 ± 0.003
Oxygen	0.1075 ± 0.0007	0.1081 ± 0.0007	1.005 ± 0.006
Average	0.1083 ± 0.0006	0.1084 ± 0.0006	1.000 ± 0.007

adequate for the formation of Ps atoms at $P(S_1)$ sites. The formation of Ps atoms in Pt.OEP molecules should therefore lead to an increase in the Doppler parameter S with increasing concentration of oxygen under UV irradiation, as is observed in figure 7(b). The solid lines in figure 7 are the least-squares fits to an expression of the form

$$\frac{S(X)}{S(X=0)} = 1 + A[X(O_2)]^{0.25}$$

where A is a constant and $X(O_2)$ is the mole fraction of oxygen in the surrounding medium. Clearly, $S(X)$ is independent of $X(O_2)$ for Mg.OEP but shows a strong dependence on $X(O_2)$ for Pt.OEP.

Concluding Remarks

Positron lifetime results by themselves do not appear to be sensitive indicators of the role of the $P(S_1)$ state in O_2 -induced quenching of the $P(T_1) \rightarrow P(S_0)$ transition in the Pt.OEP phosphor. However, concurrent Doppler broadening measurements clearly indicate a steady

increase in the probability of positronium atom formation at $P(S_1)$ sites as partial pressure of oxygen in the surrounding medium increases. The formation of $[O_2.P(S_1)]^*$ complexes at $P(S_1)$ sites decreases the population of the phosphorescing $P(T_1)$ states; thus, effectively the $P(T_1)-P(S_0)$ phosphorescence is reduced. It is, therefore, concluded that oxygen molecules quench the phosphorescence in the Pt.OEP molecules by interacting with *both* the lowest excited singlet states and the lowest excited triplet states. These conclusions are confirmed by positron annihilation measurements in nonphosphorescing Mg.OEP molecules. These results suggest that an appropriate substituent element between magnesium and platinum may provide a metalloporphyrin whose fluorescence and phosphorescence signals are equally affected by the O_2 molecules. Such a substituent may result in enhanced phosphor life under UV illumination.

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